

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number
WO 01/12545 A1

(51) International Patent Classification⁷: C01B 33/40 (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).

(21) International Application Number: PCT/EP00/07780 (81) Designated States (national): BR, CA, CN, IN, JP, KR.

(22) International Filing Date: 11 August 2000 (11.08.2000) (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/372,293 11 August 1999 (11.08.1999) US

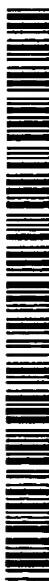
(71) Applicant: AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).

(72) Inventors: STAMIRE, Dennis; 6 Rockingham Drive, Newport Beach, CA 92660 (US). JONES, William; 6 Lantree Crescent, Cambridge CB2 2NJ (GB). PEARSON, Gregory; 1211 Goldendale Drive, Seabrook, TX 77586 (US).

Published:

— With international search report.
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/12545 A1

(54) Title: PROCESS FOR THE PREPARATION OF SMECTITES USING WATERGLASS

(57) Abstract: The present invention is directed to a process for the preparation of smectite type clays by hydrothermal treatment of a mixture containing a crystalline alumina, a divalent metal source, and waterglass. With the process according to the invention a method is provided for the direct preparation of smectite-type clays using inexpensive starting materials. Further with the process of the invention washing can often be avoided. It was further found that if waterglass is used with an additional type of silica source such as waterglass which has been ion exchanged and stabilized with ammonium ions, the surface area and sodium content of the resulting smectite-type clay can be influenced.

PROCESS FOR THE PREPARATION OF SMECTITES USING
WATERGLASS

5

The present invention is directed to a process for the preparation of smectite type clays. Smectite-type clays such as saponites and montmorillonite have several applications in the catalyst field and as absorbent. The preparation of 10 smectite type clays has been described in several patent publications. Usually smectite-type clays are prepared by reacting under hydrothermal conditions a silicon source, an aluminium source, and a magnesium source. See for instance EP-0 398 429. The silicon sources described in this publication are amorphous silica and organic silicon compounds such as 15 silicon esters and silanes. The magnesium sources described are inorganic magnesium salts, organic magnesium salts and magnesium hydroxide. The alumina sources described in this publication are aluminas such as alpha, gamma, or eta-alumina as well as various boehmite forms. Also organic aluminium salts are described such as aluminum tri-isopropylate.

20 In US 3,844,979 the preparation of saponite was described by hydrothermally treating a slurry containing aluminum trihydrate, magnesium hydroxide and an aqueous silica sol.

25 In JP 02048411 the preparation of saponites is described by hydrothermal treatment of a dispersion containing a basic magnesium carbonate such as hydromagnesite, a sodium silicate or an amorphous silica-sodium silicate mixture and sodium alumina or a non-crystalline alumina.

30 With the processes of the prior art rather expensive starting materials are used such as silica sols, amorphous silica, aluminium salts and magnesium salts. Especially organic salts are expensive starting materials. Furthermore, with the use of metal salts various ions are introduced in the smectite-type

clay, so that filtering and washing before obtaining the final product is often necessary.

With the process according to the invention a method is provided for the direct
5 preparation of smectite-type clays using inexpensive starting materials.
Further with the process of the invention washing can often be avoided.

To this end the present invention is directed to a process for the preparation of
smectite-type clays by hydrothermal treatment of a mixture containing a
10 crystalline alumina, a divalent metal source, and waterglass.

Examples of crystalline alumina are boehmite and aluminum trihydrate, which
is one of the most inexpensive alumina starting materials. Even the very crude
grades of aluminum trihydrate such as gibbsite, BOC and bauxite can be used
15 in the present process. Further, thermally treated forms of aluminium
trihydrate can be used. Also boehmite is much less expensive than aluminium
salts, especially organic aluminium salts. Further, with the use of aluminium
trihydrate, its thermally treated forms or boehmite no ions are introduced
beside OH and oxide which are the normal building blocks of smectite-type
20 clays. In the process according to the invention also mixtures of crystalline
aluminas can be used. Crystalline alumina such as aluminium trihydrate may
be pre-treated prior to the addition to the reaction mixture. Said pre-treatment
may involve treatment with acid, base treatment, thermal and/or hydrothermal
treatment, all optionally in the presence of seeds or combinations thereof. It is
25 not necessary to convert all of the aluminium source into smectite-type clay.
Any excess aluminium will be converted into silica-alumina, alumina (usually
in the form of γ alumina or (crystalline) boehmite) and/or alumina-divalent
metal during the aging step. These compounds improve the binding properties
30 of the smectite type clay and may also provide different types of desirable
functionalities. For instance, silica-alumina and alumina provide acid sites for
catalytic cracking and alumina (crystalline) boehmite also improves the nickel

encapsulation capacity. The formation of, for example, (crystalline) boehmite may be promoted by adding seeds.

Also waterglass is one of the most inexpensive silica sources known. It was 5 found that waterglass can be used in combination with the above-mentioned crystalline aluminas for the preparation of smectite-type clays. It was further found that if waterglass is used with an additional type of silica source such as waterglass which has been ion exchanged and stabilized with ammonium ions, the surface area and sodium content of the resulting smectite-type clay 10 can be influenced.

Suitable divalent metal sources for the smectite-type clay are compounds containing Mg^{2+} , Ca^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Mo^{2+} , Ni^{2+} , Fe^{2+} , Sr^{2+} , Ba^{2+} , Cu^{2+} , and mixtures of said compounds. Preferably oxides, hydroxides and carbonates of 15 these metals are used because these types of metal compounds do not introduce additional ions into the smectite-type clay, but also nitrates, chlorides, sulfates and phosphates can be used. The most preferred divalent metal source is magnesium. The preferred magnesium sources are magnesium hydroxide, magnesium oxide, magnesium hydroxy carbonate, 20 magnesium carbonate. It is not necessary to convert all of the divalent metal source smectite-type clay. Any excess magnesium will usually be converted to brucite or alumina-magnesia. For the sake of clarity, this excess of magnesium compounds in the shaped particle will be referred to in the description as magnesia. The presence of divalent metal, magnesia or 25 alumina-magnesia in the smectite-type clay may provide desirable functionalities to the clay. The presence of magnesia provides basic sites which render the shaped body suitable for removing or neutralizing strong acid streams of gases or liquids.

30 As mentioned above, the reaction is conducted under hydrothermal conditions. Within the context of this description hydrothermal means in the presence of water at a temperature above 100 °C at increased pressure.

Preferably the reaction takes place in water in an autoclave at a temperature above 100 °C, i.e. under autogeneous pressure.

The reaction mixture may be obtained by either combining slurries of the

5 starting materials or adding divalent metal source to a slurry of crystalline alumina and waterglass or vice versa. There is no need to wash or filter the product, as unwanted ions (e.g. sodium, ammonium, chloride, sulfate) which are frequently encountered when using other preparation methods, are absent in the product. If desired a preformed smectite type- clay may be added to the

10 reaction mixture. Said preformed clay may be recycled smectite-type clay from the reaction mixture or smectite-type clay made separately by the process according to the invention or any other process. The various sources can be added in any sequence. The preparation of the reaction mixture can be carried out with or without stirring, at room temperature or elevated

15 temperature. Optionally, the precursor mixture is homogenized by, for instance, milling.

Because of its simplicity, this process can be carried out in a continuous mode by mixing of a first slurry comprising crystalline alumina, a second slurry

20 comprising divalent metal source and a third containing waterglass passing the mixed slurry through a reactor vessel which can operate under hydrothermal conditions. Said first and/or second slurry and/or third slurry may be subjected to a treatment prior to mixing the slurries. Said pre-treatment may involve treatment with acid, base treatment, thermal and/or hydrothermal

25 treatment, all optionally in the presence of seeds or combinations thereof.

If desired inorganic acids and bases, for example for control of the pH, may be added to the slurry before or during reaction or to the individual reactants before combining them in the slurry. The acid and bases of choice are formic

30 acid, acetic acid, nitric acid and ammonium hydroxide, because these types of acids and bases do not introduce unwanted ions in the reaction mixture.

For some applications it is desirable to have additives, both metals and non-metals, such as rare earth metals, Si, P, B, group VI, group VIII, alkaline earth (for instance Ca and Ba) and/or transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, Sn), present. Said metals can easily be deposited on the

5 smectite-type clay. They can also be added either to the divalent metal source or the crystalline alumina, or the waterglass or to the slurry during preparation of the smectite-type clay. With the help of additives the smectite-type clay may be provided with desired functionalities, or the desired functionality may be increased by the addition of additives. The suitability of smectite-type clay for

10 the metal trapping in FCC may be improved by the addition of Zn. The presence of V and Zn improves the suitability for removal of S-compounds in the gasoline and diesel fraction of FCC.

Smectite-type clay has several applications in the catalyst field and as absorbents. For most commercial applications crystalline clays are formed into shaped bodies such as spheres. In all these applications where shaped bodies are exposed to severe processing conditions and environments, such as oil refinery applications, separations, purifications, and absorption processes, it is of paramount importance that the integrity of the smectite-type

20 clay-containing shaped bodies is kept intact and attrition is prevented. Therefore, the process of the invention also includes the shaping of the smectite-type clay. The formed smectite-type clay prepared with the process according to the invention may easily be incorporated into binder or matrix material in order to obtain attrition resistant shaped bodies. It can even be

25 shaped directly from the hydrothermally treated reaction mixture. Commonly used binder or matrix material is alumina prepared from alumina precursors such as aluminium chlorohydrol, soluble alumina salts, and acid dispersed pseudoboehmite, silica such as silica sols, silicates, silica-alumina cogels, and combinations thereof. Suitable shaping methods include spray-drying,

30 pelletising, extrusion (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the shaping mixture

or hydrothermally treated reaction mixture used for shaping should be adapted to the specific shaping step to be conducted. It might be advisable to (partially) remove the liquid used in the hydrothermally treated reaction mixture or shaping mixture and/or add additional or other liquid, and/or

5 change the pH of the mixture to make the mixture gellable and thus suitable for shaping. Various additives commonly used in the various shaping methods such as extrusion additives may be added to the precursor mixture used for shaping

10 The process according to the invention may be conducted batch-wise or in a continuous mode, optionally in a continuous multi-step operation. The process may also be conducted partly continuous and partly batch-wise

15 The smectite-type clay-containing bodies may also be prepared to contain conventional catalyst components such as matrix or filler material (e.g. clay such as kaolin, titanium oxide, zirconia, alumina, silica, silica-alumina, bentonite etcetera), molecular sieve material (e.g. zeolite Y, ZSM-5 etcetera). Said conventional catalyst components may be added prior to the shaping step. With the method according to the invention, multiply functional bodies

20 can be prepared which can be used as a catalyst or as a catalyst additive.

If desired, the smectite-type clay prepared by the process according to the invention may be subjected to ion exchange to change the chemical and physical properties of the clay. Said ion exchange can be conducted prior to

25 or after shaping. Suitable ion exchange compounds include any metal cation containing compound such as compounds containing Cu, Al, Mg, Zn, pillaring cations such as aluminum chlorohydrol, transition metals, e.g. Ni, Rare earths etcetera.

30 The present invention is further illustrated by the following examples which are not to be construed as being limitative.

EXAMPLES

Example 1

5 A slurry containing gibbsite (aluminum trihydrate), magnesium oxide and waterglass was homogenized and hydrothermally treated in an autoclave at 170 °C for 2 hours. The product was filtered and analyzed with X-ray. The XRD indicated the presence of saponite. The surface area of the saponite was 650 m²/g.

10

Example 2

Example 1 was repeated except that waterglass was used which had been ion exchanged and stabilized with ammonium ions. The resulting saponite had a 15 surface area of 550 m²/g and lower sodium content. This example shows that the surface area of the saponite can be controlled by using two different types of silica sources in the process according to the invention.

CLAIMS

- 5 1. Process for the preparation of smectite-type clays by hydrothermal treatment of a mixture containing a crystalline alumina, a divalent metal source, and waterglass.
- 10 2. Process according to claim 1 wherein the crystalline alumina is aluminum trihydrate or its thermally treated form or boehmite.
3. Process according to any one of preceding claims 1-3 wherein the divalent metal source is a magnesium compound.
- 15 4. Process according to claim 4 wherein the magnesium compound is an oxide, hydroxide, a carbonate or a mixture thereof.
5. Process according to any one of preceding claims 1-4 wherein in addition to waterglass an additional silica source is present in the mixture.
- 20 6. Process according to claim 5 wherein the additional silica source is waterglass which has been ion exchanged and stabilized with ammonium ions.
- 25 7. Process according to any one of the preceding claims 1-6 wherein the hydrothermally treated mixture is, optionally dried and, shaped.
8. Smectite-type clay-containing shaped body obtainable by the process of claim 7.

30

INTERNATIONAL SEARCH REPORT

Inten. National Application No
PCT/EP 00/07780

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B33/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 39 34 473 A (HENKEL KGAA) 18 April 1991 (1991-04-18) the whole document ---	1-4
X	EP 0 224 182 A (HOECHST AG) 3 June 1987 (1987-06-03) claim 1 page 3, line 22 - line 31 ---	1-4
A	DATABASE WPI Section Ch, Week 199013 Derwent Publications Ltd., London, GB; Class L02, AN 1990-095923 XP002153984 & JP 02 048411 A (MIZUSAWA CHEMICAL IND KK), 19 February 1990 (1990-02-19) abstract --- -/-	1-4

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the International search

11 December 2000

Date of mailing of the international search report

21/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Rigondaud, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/07780

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BE 650 582 A (NATIONAL LEAD COMPANY) 15 January 1965 (1965-01-15) page 3, paragraph 3 page 6, paragraph 2 -----	1-3
A	DE 44 05 876 A (SUED CHEMIE AG) 5 October 1995 (1995-10-05) -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 00/07780

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
DE 3934473	A 18-04-1991	NONE			
EP 0224182	A 03-06-1987	DE	3541666	A 27-05-1987	
		DE	3670277	D 17-05-1990	
		US	4749676	A 07-06-1988	
JP 2048411	A 19-02-1990	NONE			
BE 650582	A 15-01-1965	LU	46545	A 16-09-1964	
DE 4405876	A 05-10-1995	NONE			